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CUTOFF THEORY OF IMPACT BROADENING AND SHIFTING OF MICROWAVE AN--ETC(L  
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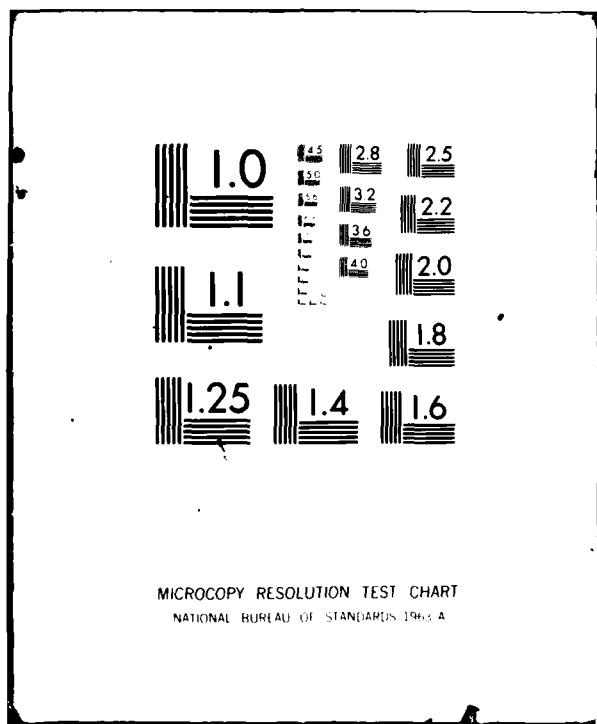
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER HDL-TR-1941	2. GOVT ACCESSION NO. HD-AC98315	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Cutoff Theory of Impact Broadening and Shifting of Microwave and Infrared Molecular Spectra		5. TYPE OF REPORT & PERIOD COVERED Technical Report
7. AUTHOR(s) Richard P. Leavitt David Korff (University of Lowell, MA)		6. PERFORMING ORG. REPORT NUMBER Mo
9. PERFORMING ORGANIZATION NAME AND ADDRESS Harry Diamond Laboratories 2800 Powder Mill Road Adelphi, MD 20783		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Program Ele: 61101A
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Materiel Development and Readiness Command Alexandria, VA 22333		12. REPORT DATE January 1981
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 55
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES DRCMS Code: 61110191A0011 HDL Project: A10033		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Molecular collisions Near-millimeter waves Spectral line shapes Pressure broadening		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) An impact theory is described for pressure broadening and shifting of rotation-vibration lines using a natural cutoff. The theory is based on Anderson's theoretical framework and employs an exponential expansion of the collision matrix elements derived from a linked cluster theorem for degenerate states. The final expression for the interruption function is similar in form to Gordon's semiclassical interruption function. Closed-form		

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20. ABSTRACT (Cont'd)

expressions for the broadening and shift cross sections are given for exactly resonant dipole-dipole collisions, and an exact calculation for the HCl self-broadening in the 0 to 2 vibrational band.

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## 1. INTRODUCTION

Since the publication of Anderson's classic paper,<sup>1</sup> questions concerning impact theories of pressure broadening in the microwave and infrared regions have shifted from the realm of the foundations of the impact theory. Attention is now concentrated on such areas as the convergence of the various terms in Anderson's expansion and the extension of the theory to include broadening of vibration-rotation lines, as well as the pure rotation lines addressed by Anderson. The solutions of these problems, particularly the former, have not been entirely satisfactory. Several *ad hoc* cutoffs have been introduced into Anderson's theory,<sup>1-3</sup> and although these have agreed well with each other and with experiment, their differences are sufficient to warrant further examination.

In an attempt to resolve these problems, Murphy and Boggs<sup>4</sup> have developed a theory which begins with a different theoretical framework from Anderson's, and which introduces a natural cutoff from the outset. This theory has several drawbacks, however. First, the cutoff depends on the azimuthal quantum numbers of the radiating and perturbing molecules. This requires an involved machine computation to evaluate certain  $m$ -sums occurring in the theory. Second, the theoretical foundation of the theory is not as clear as that of Anderson; no off-diagonal matrix elements of the time-evolution operator occur in Murphy and Boggs' theory, and it is not clear how these are to be introduced into their framework.

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<sup>1</sup>P. W. Anderson, *Phys. Rev.*, 76 (1949), 647.

<sup>2</sup>P. W. Anderson, PhD Dissertation, Harvard University (1949).

<sup>3</sup>R. D. Sharma and G. E. Caledonia, *J. Chem. Phys.*, 54 (1970), 434.

<sup>4</sup>J. S. Murphy and J. E. Boggs, *J. Chem. Phys.*, 47 (1967), 691.

Gordon has given a nonperturbative semiclassical theory,<sup>5</sup> which includes all the important effects of molecular collisions: phase shifts, inelastic collisions, and molecular reorientation (the Murphy-Boggs theory does not include the third of these effects). However, in order to evaluate pressure-broadening cross sections from his theory, Gordon is forced into a rough guess for the probability of elastic collisions (because he treats the angular momentum as a continuous variable). Thus, Gordon's theory, while satisfactory from a theoretical point of view, does not allow accurate calculations of pressure shifts and broadening.

What we propose is an impact theory of pressure broadening and shift, based on Anderson's framework, and containing a natural,  $m$ -independent cutoff. The theory is similar to that of Murphy and Boggs, except that it explicitly exhibits the correct rotational symmetry. The theory is expressed from the outset in terms of the group-theoretical properties of the interaction Hamiltonian between the radiating and perturbing molecules. In this way it is possible to formulate the theory in a very general manner, allowing for complicated interactions between the two molecules. The final form of the theory is shown to be similar to the form of the semiclassical theory of Gordon.

Our starting point will be the general relations given by Anderson<sup>1</sup> and rederived by Tsao and Curnutte.<sup>6</sup> In particular, we use equations (79) and (80) of Tsao and Curnutte:

$$\Delta v = \frac{nv}{2\pi c} \sigma_i \text{ cm}^{-1} \quad (1)$$

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<sup>1</sup>P. W. Anderson, *Phys. Rev.*, 76 (1949), 647.

<sup>5</sup>R. G. Gordon, *J. Chem. Phys.*, 44 (1966), 3083.

<sup>6</sup>C. J. Tsao and B. Curnutte, *J. Quant. Spectr. Rad. Trans.*, 2 (1962), 41.

for the line shift, and

$$(\Delta v)_{1/2} = \frac{nv}{2\pi c} \sigma_r \text{ cm}^{-1} \quad (2)$$

for the pressure-broadened half-width. In the above,  $n$  is the perturber density and  $v$  is the relative velocity between colliding molecules. The question of averaging equations (1) and (2) over a Maxwell-Boltzmann distribution of relative velocities will be addressed later. For now, we simply take  $v$  as the average velocity.

Anderson gives the following expression for the cross section:

$$\sigma = \sigma_r + i\sigma_i = \sum_{J_2} \rho_{J_2 J_2} \sigma_{J_2} \quad , \quad (3)$$

where

$$\sigma_{J_2} = 2\pi \int_0^\infty b \, db \, S_{J_2}(b) \quad , \quad (4)$$

and where  $J_2$  is the rotational angular momentum of the perturbing molecule, and  $b$  is the impact parameter. The latter two equations are equations (74) and (87) of Tsao and Curnutte.<sup>6</sup> The quantity  $\rho_{J_2 J_2}$  is a diagonal element of the density matrix for the perturber, given by

$$\rho_{J_2 J_2} = \left(2J_2 + 1\right) \exp\left[-\epsilon_{J_2}/kT\right] / \sum_{J_2} \left(2J_2 + 1\right) \exp\left[-\epsilon_{J_2}/kT\right] \quad , \quad (5)$$

<sup>6</sup>C. J. Tsao and B. Curnutte, *J. Quant. Spectr. Rad. Trans.*, 2 (1962)  
41.

where  $\epsilon_{J_2}$  is the energy of the perturber rotational state  $J_2$ . The function  $S_{J_2}(b)$  is given by equation (88) of Tsao and Curnutte:

$$S(b) = 1 - \sum_{\substack{\text{all } M \\ J_2'}} \frac{\langle J_f(M_f) 1(M) | J_i(M_i) \rangle \langle J_f(M'_f) 1(M) | J_i(M'_i) \rangle}{(2J_i + 1)(2J_2 + 1)} \times \langle J_f M_f J_2 M_2 | T^{-1}(b) | J_f M'_f J'_2 M'_2 \rangle \langle J_i M'_i J'_2 M'_2 | T(b) | J_i M_i J_2 M_2 \rangle . \quad (6)$$

In the above, the subscripts  $i$  and  $f$  refer to initial and final states of the radiative transition, and primed and unprimed quantities refer to states after and before the collision, respectively. The quantity  $\langle J_f(M_f) 1(M) | J_i(M_i) \rangle$  is an unsymmetrized vector-coupling coefficient (Clebsch-Gordan coefficient), and  $T(b)$  is the time-evolution operator for collisions with an impact parameter  $b$ . This operator obeys the differential equation

$$i\hbar \frac{dT(b;t)}{dt} = \tilde{V}(b;t) T(b;t) , \quad (7)$$

subject to the initial condition

$$T(b;-\infty) = 1 \quad (8)$$

and

$$T(b) \equiv T(b,\infty) . \quad (9)$$

$\tilde{V}(t)$  is the interaction Hamiltonian between radiator and perturber in the interaction representation

$$\tilde{V}(b,t) = \exp[-H_0 t / i\hbar] V(t) \exp[H_0 t / i\hbar] , \quad (10)$$

where  $H_0$  is the unperturbed Hamiltonian  $[H_0(1) + H_0(2)]$  of radiator and perturber. The operator  $V(t)$  is given in terms of operators depending on molecules 1 and 2 (radiator and perturber, respectively), and contains an explicit time dependence due to the changing distance and relative orientation between the two molecules. This is the classical path assumption. We have suppressed the  $b$ -dependence in  $V(t)$ ; such dependence will be understood throughout the following.

We take equations (1) through (10) as our starting points, as does Anderson's theory. However, Anderson goes one step further and solves (7) via the usual perturbation method. He obtains

$$\langle m | T(b) | n \rangle = \delta_{mn} + \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt_1 \langle m | \tilde{V}(t_1) | n \rangle \quad (11)$$

$$+ \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \sum_k \langle m | \tilde{V}(t_1) | k \rangle \langle k | \tilde{V}(t_2) | n \rangle + \dots$$

where we have used the shorthand notation  $(m)$  to stand for the states  $(J_1 M_1 J_2 M_2)$ . Anderson substitutes expression (11) into equation (6) to obtain his final result for  $S_{J_2}(b)$ . When this expression is used, the integral of equation (4) over impact parameter diverges due to the small  $b$  behavior of the T-matrix elements.

In order to remove this divergence in a natural manner (i.e., without introducing any additional *ad hoc* assumptions), we shall obtain an alternative expansion to (11) for the matrix elements of the  $T(b)$  operator. To do this we examine the rotational and time-reversal symmetries of the interaction Hamiltonian and the consequences of these symmetries for a  $T$ -matrix element with an exponential cutoff factored out. By matching this exponential expansion with the expansion of equation (11), we can unambiguously determine all the terms in the expansion. We also show that the exponential expansion is equivalent to summing all closed-loop graphs in a graphical representation of the theory by use of a linked cluster theorem.

## 2. GENERAL DERIVATION

### 2.1 Properties of $T$ -matrix

We begin our derivation of the exponential cutoff theory by postulating the following form for the  $T$ -matrix elements.

$$\langle J'_1 M'_1 J'_2 M'_2 | T | J_1 M_1 J_2 M_2 \rangle = A_{J'_1 M'_1 J'_2 M'_2; J_1 M_1 J_2 M_2} \quad (12)$$

$$\times \exp [B_{J'_1 M'_1 J'_2 M'_2; J_1 M_1 J_2 M_2}]$$

where the quantities  $A$  and  $B$  are yet to be determined. As in the introduction, we explicitly label the states according to their rotational properties; vibrational and electronic quantum numbers will be suppressed in what follows. We also assume that  $A$  and  $B$  are expanded in a power series in the interaction potential. If the right-hand side

of equation (12) were expanded out and matched term by term with expression (11), a system of equations would result for the  $A^{(n)}$  and  $B^{(n)}$  [ $A^{(n)}$  represents the  $n^{\text{th}}$  term in the power-series expansion for  $A$ , and similarly for  $B^{(n)}$ ]. However, the first  $n$  of these equations would contain  $2n$  unknowns; that is,  $A^{(k)}$  and  $B^{(k)}$  for  $k = 0, 1, \dots, n-1$ . Therefore, some other conditions on the  $A^{(n)}$  and  $B^{(n)}$  are necessary to determine them uniquely.

First we note that equation (12) must be substituted into equation (6) to obtain  $S(b)$ , and summations must be carried out over the  $M$  quantum numbers. To do this in closed form, the  $M$  dependence in (12) must be of the form of vector-coupling coefficients or products of vector-coupling coefficients, and these must occur in  $A$  and not in  $B$ . If this is the case, we may use the well-known properties of the V-C coefficients to carry out the  $M$ -summations. Therefore, we postulate the relation

$$B_{J'_1 M'_1 J'_2 M'_2; J_1 M_1 J_2 M_2} = B_{J'_1 J'_2; J_1 J_2} \text{ only} \quad . \quad (13)$$

This relation implies that the quantity  $B_{J'_1 J'_2; J_1 J_2}$  is rotationally invariant; in the language of group theory, it is constructed from combinations of the interaction Hamiltonian which transform like irreducible tensors of rank zero under rotations of molecule 1 or molecule 2.

For our second relation, we examine the time-reversal symmetry of the interaction Hamiltonian. We assume that the interaction Hamiltonian may be expanded in terms of spherical harmonics in the vector  $R(t)$  between the two molecules.

$$V(t) = \sum_{L, \mu} A^{L, \mu t} (1, 2) Y_{L\mu} [\theta(t), \phi(t)] f_L [R(t)] \quad (14)$$

where  $A^{L, \mu t} (1, 2)$  is a time-independent operator.

To study the time-reversal properties of (14), we must make some assumptions about the path of molecule 2. It is usually assumed that the molecule travels in a straight line relative to molecule 1; this is usually a good approximation. However, we need not be so stringent, since we wish to keep the theory as general as possible. We shall assume, however, that the translational motion of the two molecules is governed by central forces, and that the noncentral part of the potential will have negligible effect on the translational motion. If this is the case, then the orbit of molecule 2 relative to molecule 1 will be symmetric about the point of closest approach, which we label by the vector  $\underline{r}_0$ . To demonstrate the effect of this orbit symmetry on the symmetry of the interaction Hamiltonian (14), we construct a specific coordinate system in which the z-axis is coincident with the vector  $\underline{r}_0$  and the motion of molecule 2 is in the y-z plane. We also take the vector  $\underline{R}(0) = \underline{r}_0$  so that the orbit is symmetric about the time  $t = 0$  in the following way.

$$\underline{R}(-t) = \underline{R}(t) \quad (15a)$$

$$\theta(-t) = \theta(t) \quad (15b)$$

$$\phi(-t) = \phi(t) + \pi \quad , \quad (15c)$$

where  $\theta(t)$  and  $\phi(t)$  are the usual polar angles of the vector  $\mathbf{R}(t)$  with respect to the coordinate system. For this special choice of coordinate system, we have

$$v_{L\mu}^* [\theta(-t), \phi(-t)] = v_{L\mu} [\theta(t), \phi(t)] \quad . \quad (16)$$

Therefore

$$\langle J'_1 M'_1 J'_2 M'_2 | \tilde{v}(-t) | J_1 M_1 J_2 M_2 \rangle^* \quad (17)$$

$$= \langle J'_1 M'_1 J'_2 M'_2 | \tilde{v}(t) | J_1 M_1 J_2 M_2 \rangle \quad .$$

To see the consequences of this relation, we examine the perturbation expansion, (11). By reversing the order of integrations and by using the hermiticity relation,

$$\langle n | \tilde{v}(t) | m \rangle = \langle m | \tilde{v}(t) | n \rangle^* \quad , \quad (18)$$

and by changing the signs of all the integration variables, we arrive at the relation

$$\begin{aligned} \langle n | T | m \rangle &= \delta_{nm} + \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt_1 \langle m | \tilde{v}(-t_1) | n \rangle^* + \\ &+ \left( \frac{1}{i\hbar} \right)^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \sum_k \langle m | \tilde{v}(-t_1) | k \rangle^* \langle k | \tilde{v}(-t_2) | n \rangle^* + \dots \end{aligned} \quad (19)$$

Substitution of (17) into (19) yields the relation

$$\langle J'_1 M'_1 J'_2 M'_2 | T | J_1 M_1 J_2 M_2 \rangle = \langle J_1 M_1 J_2 M_2 | T | J'_1 M'_1 J'_2 M'_2 \rangle . \quad (20)$$

Referring to equation (12), we demand that (20) hold separately for each of the quantities A and B. The relation (20) holds for T only in the specific coordinate system described above. However, since B is rotationally invariant, the symmetry (20) will hold for B in any coordinate system, and we may write

$$B_{J'_1 J'_2; J_1 J_2} = B_{J_1 J_2; J'_1 J'_2} . \quad (21)$$

Having determined the symmetry of B upon exchange of initial and final states we now impose a futher requirement

$$B_{J'_1 J'_2; J_1 J_2} = (B_{J_1 J_2} + B_{J'_1 J'_2}) / 2 . \quad (22)$$

which satisfies (21) and has the additional property that the B part of the T-matrix factors into two parts, one involving the initial state and the other involving the final state. Equation (22) is convenient, but not absolutely necessary to the development of the theory. This somewhat arbitrary decomposition will be shown below, in any event, to affect only a restricted class of contributions to the interruption function S(b).

In order to obtain a condition on the A's, we investigate the rotational properties of the T-matrix. We assume that T may be expanded in terms of unit irreducible tensors in the spaces of particles 1 and 2:

$$T = \sum_{\substack{k_1 q_1 \\ k_2 q_2}} T^{k_1 k_2} U_{q_1}^{k_1(1)} U_{q_2}^{k_2(2)} . \quad (23)$$

(These unit tensors are defined such that the reduced matrix elements between any states are unity.) We may then calculate the matrix elements of T:

$$\begin{aligned} \langle J_1^{\prime} M_1^{\prime} J_2^{\prime} M_2^{\prime} | T | J_1 M_1 J_2 M_2 \rangle &= \sum_{k_1 k_2} \langle J_1^{\prime} J_2^{\prime} | | T^{k_1 k_2} | | J_1 J_2 \rangle \\ &\times \langle J_1 (M_1) k_1 (M_1' - M_1) | J_1^{\prime} M_1^{\prime} \rangle \langle J_2 (M_2) k_2 (M_2' - M_2) | J_2^{\prime} M_2^{\prime} \rangle . \end{aligned} \quad (24)$$

And we may perform a sum over the M's to obtain

$$\begin{aligned} \sum_{M_1 M_2} \langle J_1 M_1 J_2 M_2 | T | J_1 M_1 J_2 M_2 \rangle \\ = (2J_1 + 1)(2J_2 + 1) \langle J_1 J_2 | | T^{00} | | J_1 J_2 \rangle . \end{aligned} \quad (25)$$

This states the well-known result that the average of the diagonal matrix elements of an operator within the subspace  $(J_1 J_2)$  is equal to the part of the operator which is invariant under rotations; i.e., a scalar in the separate spaces of molecules 1 and 2. We impose the constraint that

$$\sum_{M_1 M_2} A_{J_1 M_1 J_2 M_2; J_1 M_1 J_2 M_2}^{(n)} = (2J_1 + 1)(2J_2 + 1) \delta_{n0} , \quad (26)$$

where  $A^{(n)}$  is the  $n^{\text{th}}$  order term in the power series expansion of  $A$ , and that the zeroth order term  $A^{(0)}$  is invariant under rotations (is in fact equal to the unit matrix). All the other terms in the expansion of  $A$  contain no part which is invariant under rotations. Referring again to equation (12), we see that (25) and (26) imply

$$\exp[B_{J_1 J_2}] = \langle J_1 J_2 | | T^{00} | | J_1 J_2 \rangle . \quad (27)$$

Therefore,  $B_{J_1 J_2}$  is an exponential expansion of the rotationally invariant portion of the  $T$ -matrix element.

## 2.2 Evaluation of Various Terms in Expansion

We are now in a position to evaluate the various  $A^{(n)}$  and  $B^{(n)}$ . By expanding the exponential in (12) to the  $n^{\text{th}}$  order and matching the  $k^{\text{th}}$  order terms obtained thereby with the  $k^{\text{th}}$  order term in equation (11), we find

$$[A_{mk} \exp\{B_{mk}\}]_n = \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{t_{n-1}} dt_n \left(\frac{1}{im}\right)^n$$

(28)

$$\times \sum_{l, p, \dots} \langle_m | \tilde{v}(t_1) | l \rangle \cdots \langle_p | \tilde{v}(t_n) | k \rangle ,$$

where  $[\cdot]_n$  means the  $n^{\text{th}}$  term in the expansion of the quantity within the brackets. This equation, together with equations (22) and (26), is sufficient to determine the  $A^{(n)}$  and  $B^{(n)}$  to arbitrary order. We shall evaluate the quantity  $A$  to first order and  $B$  to second order, and then

state a general prescription for arbitrary order (the reason for evaluating A to one less order than B will become clear shortly).

We set  $B^{(0)} = 0$ . Then we obtain

$$A_{J'_1 M'_1 J'_2 M'_2; J_1 M_1 J_2 M_2}^{(0)} = \delta_{J'_1 J'_1} \delta_{J'_2 J'_2} \delta_{M'_1 M'_1} \delta_{M'_2 M'_2} , \quad (29)$$

as stated earlier. The first-order term gives

$$\begin{aligned} A_{J'_1 M'_1 J'_2 M'_2; J_1 M_1 J_2 M_2}^{(1)} &= \delta_{J'_1 J'_1} \delta_{J'_2 J'_2} \delta_{M'_1 M'_1} \delta_{M'_2 M'_2} B_{J'_1 J'_1}^{(1)} \\ &= \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt_1 \langle J'_1 M'_1 J'_2 M'_2 | \tilde{v}(t_1) | J_1 M_1 J_2 M_2 \rangle . \end{aligned} \quad (30)$$

Setting  $(J'_1 J'_2 M'_1 M'_2) = (J_1 J_2 M_1 M_2)$  and summing over  $M_1$  and  $M_2$ , making use of equation (26), yields

$$\begin{aligned} B_{J_1 J_2}^{(1)} &= \frac{1}{(2J_1 + 1)(2J_2 + 1)} \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt_1 \\ &\times \sum_{M_1 M_2} \langle J_1 M_1 J_2 M_2 | \tilde{v}(t_1) | J_1 M_1 J_2 M_2 \rangle , \end{aligned} \quad (31)$$

which, when substituted back into (30), gives the following expression for the first-order term in A.

$$A_{J'_1 M'_1 J'_2 M'_2; J_1 M_1 J_2 M_2}^{(1)} = \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt_1 \quad (32)$$

$$\times \langle J'_1 M'_1 J'_2 M'_2 | \tilde{V}(t_1) | J_1 M_1 J_2 M_2 \rangle - \frac{\delta_{J'_1 J'_2} \delta_{J'_2 J'_2} \delta_{M'_1 M'_1} \delta_{M'_2 M'_2}}{(2J'_1 + 1)(2J'_2 + 1) i\hbar}$$

$$\times \int_{-\infty}^{\infty} dt_1 \sum_{M'_1 M'_2} \langle J'_1 M'_1 J'_2 M'_2 | \tilde{V}(t_1) | J_1 M_1 J_2 M_2 \rangle \quad .$$

For the second-order term we have

$$\begin{aligned} & A_{J'_1 M'_1 J'_2 M'_2; J_1 M_1 J_2 M_2}^{(2)} + \left[ B_{J'_1 J'_2}^{(1)} + B_{J'_1 J'_2}^{(1)} \right] / 2 \\ & \times A_{J'_1 M'_1 J'_2 M'_2; J_1 M_1 J_2 M_2}^{(1)} + \delta_{J'_1 J'_1} \delta_{J'_2 J'_2} \delta_{M'_1 M'_1} \delta_{M'_2 M'_2} \\ & \times \frac{1}{2} \left[ B_{J'_1 J'_2}^{(1)2} + B_{J'_1 J'_2}^{(2)} \right] = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \left( \frac{1}{i\hbar} \right)^2 \sum_{\substack{J''_1 J''_2 \\ M''_1 M''_2}} \\ & \times \langle J'_1 M'_1 J'_2 M'_2 | \tilde{V}(t_1) | J''_1 M''_1 J''_2 M''_2 \rangle \\ & \times \langle J''_1 M''_1 J''_2 M''_2 | \tilde{V}(t_2) | J_1 M_1 J_2 M_2 \rangle \quad , \end{aligned} \quad (33)$$

from which we may obtain  $B^{(2)}$  by a procedure analogous to that used to obtain  $B^{(1)}$ .

$$\begin{aligned} B_{J'_1 J'_2}^{(2)} &= \frac{1}{(2J'_1 + 1)(2J'_2 + 1)} \left( \frac{1}{i\hbar} \right)^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \sum_{\substack{J''_1 J''_2 \\ \text{all } M}} \\ & \times \langle J'_1 M'_1 J'_2 M'_2 | \tilde{V}(t_1) | J''_1 M''_1 J''_2 M''_2 \rangle \\ & \times \langle J''_1 M''_1 J''_2 M''_2 | \tilde{V}(t_2) | J_1 M_1 J_2 M_2 \rangle - B_{J'_1 J'_2}^{(1)2} / 2 \quad , \end{aligned} \quad (34)$$

and we may substitute this expression back into equation (33) to obtain an expression for  $A^{(2)}$ .

It is now clear how to obtain the  $k^{\text{th}}$  approximation for  $A$  and  $B$ . We simply write down equation (28) for the  $k^{\text{th}}$  approximation, set  $(J_1' J_2' M_1' M_2') = (J_1 J_2 M_1 M_2)$  and sum over  $M_1$  and  $M_2$ . This gives a relation analogous to (34) for the  $B^{(k)}$  in terms of known quantities and the  $B$ 's already calculated. Substitution of the resulting expression into (27) gives the  $A^{(k)}$ . One may proceed in this manner to any desired order in the expansion. We shall stop here, however, and calculate  $S(b)$  in terms of the  $A^{(k)}$  and  $B^{(k)}$ .

### 2.3 Evaluation of $S(b)$

We now substitute our expansion of the T-matrix into equation (6) to obtain an expression for  $S(b)$ . To do this, we need the matrix elements of  $T^{-1}(b)$ , which are obtained from those of  $T(b)$  by unitarity.

$$\begin{aligned} & \langle J_1' M_1' J_2' M_2' | T^{-1}(b) | J_1 M_1 J_2 M_2 \rangle \\ & = \langle J_1 M_1 J_2 M_2 | T(b) | J_1' M_1' J_2' M_2' \rangle^* \quad . \end{aligned} \tag{35}$$

Substituting the expansion (12) for the T-matrix, we first consider all the terms which contain a factor  $A^{(0)}$ . For these we may use the unitarity of the V-C coefficients and equation (26) to perform the  $M$ -sums explicitly. All the other terms must be handled separately, one at a time. With this in mind, we arrive at the following result for  $S(b)$ :

$$\begin{aligned}
S(b) &= 1 - \exp \left[ B_{J_f J_2}^* + B_{J_i J_2} \right] \\
&- \sum_{\substack{J_2 \\ \text{all } M}} \frac{\langle J_f(M_f) 1(M) | J_i(M_i) \rangle \langle J_f(M_f') 1(M) | J_i(M_i') \rangle}{(2J_i + 1)(2J_2 + 1)} \\
&\times \left[ A_{J_f M_f' J_2 M_2}^{(1)*} + A_{J_f M_f' J_2 M_2}^{(2)*} + \dots \right] \\
&\times \left[ A_{J_i M_i' J_2 M_2}^{(1)} + A_{J_i M_i' J_2 M_2}^{(2)} + \dots \right] \\
&\times \exp \left[ \frac{1}{2} \left\{ B_{J_f J_2}^* + B_{J_f J_2}^* + B_{J_i J_2} + B_{J_i J_2} \right\} \right] . \tag{36}
\end{aligned}$$

The main contribution to equation (36) arises from the first two terms, the last term being a small correction. In fact, it is only the last term which is sensitive to the decomposition (22). Note also that equation (36) is valid to all orders of perturbation theory, and that contributions to  $S(b)$  in the  $n^{\text{th}}$  order come from the  $A^{(k)}$  with  $k \leq (n - 1)$ , as noted earlier.

### 3. EVALUATION OF $S(b)$ FOR HARMONIC EXPANSION OF POTENTIAL

In order to make the maximum use of the formalism we have developed, we shall use the group theoretical properties of the interaction Hamiltonian. This Hamiltonian may be written in terms of spherical tensors as follows:

$$v(t) = \sum_{\substack{k_1 k_2 k \\ \mu_1 \mu_2}} v_{k_1 k_2 k} [R(t)] c_{k_1 \mu_1}^{(1)} c_{k_2 \mu_2}^{(2)} (37)$$

$$x c_{k, \mu_1}^{\dagger} + \mu_2 \left[ \hat{R}(t) \right] \langle k_1(\mu_1) k_2(\mu_2) | k(\mu_1 + \mu_2) \rangle ,$$

where the  $c_{k\mu}$  are defined by

$$c_{k\mu}(\hat{r}) = \left[ \frac{4\pi}{2k+1} \right]^{1/2} Y_{k\mu}(\hat{r}) , \quad (38)$$

and where  $Y_{k\mu}$  is the ordinary spherical harmonic. Equation (37) is the most general form for the interaction potential allowed by the rotational invariance of the system; that is, if we rotate the coordinates of molecule 1 and molecule 2 and also the vector  $\hat{R}(t)$  between the two by the same rotation, the interaction potential must remain unchanged. In addition, invariance under coordinate inversion requires that  $k_1 + k_2 + k$  be even.

As an example of equation 37, we have the usual electrostatic multipolar expansion, wherein

$$v_{k_1 k_2 k} [R(t)] = \left[ \frac{(2k_1 + 2k_2)!}{(2k_1)!(2k_2)!} \right]^{1/2} (-1)^{k_2} q_{k_1}^{(1)} q_{k_2}^{(2)} (39)$$

$$x R(t)^{-k_1-k_2-1} \delta_{k, k_1 + k_2} ,$$

where  $q_k$  is a multipolar moment (i.e.,  $q_1$  is the dipole moment,  $q_2$  is the quadrupole moment, etc.).

The required matrix elements of the interaction potential are given by

$$\begin{aligned}
 & \langle J_1^M J_2^M | \tilde{V}(t) | J_1^{M_1} J_2^{M_2} \rangle \\
 &= \exp \left[ i(\omega_{J_1^M J_2^M} - \omega_{J_1 J_2}) t \right] \sum_{\substack{k_1 k_2 k \\ \mu_1 \mu_2}} v_{k_1 k_2 k} [R(t)] \\
 & \times \left[ \frac{(2J_1 + 1)(2J_2 + 1)}{(2J_1^M + 1)(2J_2^M + 1)} \right]^{1/2} \langle J_1(0) k_1(0) | J_1^M(0) \rangle \\
 & \times \langle J_2(0) k_2(0) | J_2^M(0) \rangle \langle J_1(M_1) k_1(\mu_1) | J_1^M(M_1) \rangle \\
 & \times \langle J_2(M_2) k_2(\mu_2) | J_2^M(M_2) \rangle \langle k_1(\mu_1) k_2(\mu_2) | k(\mu_1 + \mu_2) \rangle \\
 & \times c_{k, \mu_1 + \mu_2}^{\dagger} \hat{R} . \tag{40}
 \end{aligned}$$

We now substitute this expression for the matrix elements into equations (31), (32), and (33) to obtain the  $A_{J_1 J_2}^{(n)}$  and  $B_{J_1 J_2}^{(n)}$ . First, we consider the  $B_{J_1 J_2}^{(2)}$ . The first-order term (32) is obtained simply by summing equation (4) over the  $M$ 's:

$$B_{J_1 J_2}^{(2)} = \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt v_{000} [R(t)] = -i\Delta_{J_1 J_2}^{(1)} . \tag{41}$$

For the second-order term we substitute the matrix elements into (34) to obtain

$$\begin{aligned}
 B_{J_1 J_2}^{(2)} &= \frac{1}{(i\hbar)^2 (2J_1 + 1)(2J_2 + 1)} \sum_{\substack{k_1 k_2 k \\ J_1'' J_2'' \mu}} \int_{-\infty}^{\infty} dt_1 \\
 &\times \int_{-\infty}^{t_1} dt_2 \exp \left[ i(\omega_{J_1 J_2} - \omega_{J_1'' J_2''})(t_1 - t_2) \right] v_{k_1 k_2 k}(t_1) \quad (42) \\
 &\times v_{k_1' k_2' k'}(t_2) \langle J_1(0) k_1(0) | J_1''(0) \rangle \langle J_1''(0) k_1(0) | J_1(0) \rangle \\
 &\times \langle J_2(0) k_2'(0) | J_2''(0) \rangle \langle J_2''(0) k_2(0) | J_2(0) \rangle \\
 &\times \langle J_1(M_1) k_1'(-\mu_1) | J_1''(M_1 - \mu_1) \rangle \langle J_1''(M_1 - \mu_1) k_1(\mu_1) | J_1(M_1) \rangle \\
 &\times \langle J_2(M_2) k_2'(-\mu_2) | J_2''(M_2 - \mu_2) \rangle \langle J_2''(M_2 - \mu_2) k_2(\mu_2) | J_2(M_2) \rangle \\
 &\times \langle k_1(\mu_1) k_2(\mu_2) | k(\mu_1 + \mu_2) \rangle \langle k_1'(-\mu_1) k_2'(-\mu_2) | k'(-\mu_1 - \mu_2) \rangle \\
 &\times c_{k, \mu_1 + \mu_2}^{\dagger} \left[ \hat{R}(t_1) \right] c_{k', -\mu_1 - \mu_2}^{\dagger} \left[ \hat{R}(t_2) \right] - B_{J_1 J_2}^{(1)2}/2
 \end{aligned}$$

Now all  $M$ -summations but one may be performed using the unitarity of the V-C coefficients to obtain

$$\begin{aligned}
 B_{J_1 J_2}^{(2)} &= \left( \frac{1}{i\hbar} \right)^2 \sum_{\substack{k_1 k_2 k \\ J_1'' J_2'' \mu}} \frac{\langle J_1(0) k_1(0) | J_1''(0) \rangle^2 \langle J_2(0) k_2(0) | J_2''(0) \rangle^2}{(2k_1 + 1)(2k_2 + 1)} \\
 &\times \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \exp \left[ i(\omega_{J_1 J_2} - \omega_{J_1'' J_2''})(t_1 - t_2) \right] v_{k_1 k_2 k}(t_1) \quad (43) \\
 &\times v_{k_1 k_2 k}(t_2) c_{k \mu}^{\dagger} \left[ \hat{R}(t_1) \right] c_{k \mu} \left[ \hat{R}(t_2) \right] - B_{J_1 J_2}^{(1)2}/2
 \end{aligned}$$

In order to perform the indicated time integrations, we introduce the Fourier transform of the interaction potential:

$$v_{k\mu}^{k_1 k_2}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} v_{k_1 k_2 k}(t) C_{k\mu}[\hat{R}(t)] . \quad (44)$$

Introducing this into equation (43) allows the time integrations to be performed. Therefore, equation (43) reduces to

$$B_{J_1 J_2}^{(2)} = -S_{J_1 J_2}^{(2)outer} - i\Delta_{J_1 J_2}^{(2)} + \frac{1}{2} \Delta_{J_1 J_2}^{(1)2} , \quad (45)$$

where

$$S_{J_1 J_2}^{(2)outer} = \frac{1}{2} \sum_{\substack{J_1'' J_2'' \mu \\ k_1 k_2 k}} \frac{\langle J_1(0) k_1(0) | J_1''(0) \rangle^2}{2k_1 + 1} \frac{\langle J_2(0) k_2(0) | J_2''(0) \rangle^2}{2k_2 + 1} \quad (46)$$

$$\times \langle J_1(0) k_1(0) | J_1''(0) \rangle^2 \frac{1}{\pi^2} \left| v_{k\mu}^{k_1 k_2} (J_1'' J_2'' - J_1 J_2) \right|^2$$

and

$$\Delta_{J_1 J_2}^{(2)} = \frac{1}{2\pi} \sum_{\substack{J_1'' J_2'' \mu \\ k_1 k_2 k}} \frac{\langle J_1(0) k_1(0) | J_1''(0) \rangle^2 \langle J_2(0) k_2(0) | J_2''(0) \rangle^2}{(2k_1 + 1)(2k_2 + 1)} \quad (47)$$

$$\times \frac{1}{\pi^2} P \int_{-\infty}^{\infty} d\omega \left( \omega_{J_1 J_2} - \omega_{J_1'' J_2''} + \omega \right)^{-1} \left| v_{k\mu}^{k_1 k_2}(\omega) \right|^2$$

and where  $\Delta_{J_1 J_2}^{(1)}$  is given by equation (41):

$$\Delta_{J_1 J_2}^{(1)} = \frac{1}{\hbar} v_{00}^{00}(0) . \quad (48)$$

All the B's have now been evaluated to second order. What remains is the last term in equation (36), the so-called correction term. To second order in the interaction potential, we have

$$\begin{aligned} s_{J_i J_f; J_2}^{(2)corr} = & - \sum_{\substack{J_2 \\ \text{all } M}} \frac{\langle J_f(M_f) | J_i(M_i) \rangle \langle J_f(M'_f) | J_i(M'_i) \rangle}{(2J_i + 1)(2J_f + 1)} \\ & \times A_{J_f M_f J'_2 M'_2; J_f M_f J'_2 M'_2}^{(1)} A_{J_i M_i J'_2 M'_2; J_i M_i J'_2 M'_2}^{(1)} \\ & \times \exp \left[ \frac{1}{2} \left\{ B_{J_f J_2}^* + B_{J_f J'_2}^* + B_{J_i J_2} + B_{J_i J'_2} \right\} \right] . \end{aligned} \quad (49)$$

We may now insert equation (31) into this to obtain

$$\begin{aligned} s_{J_i J_f; J_2}^{(2)corr} = & \frac{1}{\hbar^2} \sum_{\substack{J'' \\ \substack{2 \\ \text{all } M}}} \frac{\langle J_f(M_f) | J_i(M_i) \rangle}{(2J_i + 1)(2J''_2 + 1)} \\ & \times \langle J_f(M'_f) | J_i(M'_i) \rangle \exp \left[ \frac{1}{2} \left\{ B_{J_f J_2}^* + B_{J_f J''_2}^* + B_{J_i J_2} + B_{J_i J''_2} \right\} \right] \\ & \times \int_{-\infty}^{\infty} dt_1 \langle J_f M_f J'_2 M'_2 | \tilde{v}(t_1) | J_f M_f J'_2 M'_2 \rangle^* \\ & \times \int_{-\infty}^{\infty} dt_2 \langle J_i M_i J'_2 M'_2 | \tilde{v}(t_2) | J_i M_i J'_2 M'_2 \rangle \\ & + \Delta_{J_i J_2}^{(1)} \Delta_{J_f J_2}^{(1)} \exp \left[ B_{J_f J_2}^* + B_{J_i J_2} \right] . \end{aligned} \quad (50)$$

The matrix elements (40) may be substituted into the above and the M-summations performed by standard methods. The result is

$$\begin{aligned}
 S_{J_i J_f; J_2}^{(2)corr} &= \sum_{J'_2} S_{J_i J_f; J_2 J'_2}^{(2)middle} \\
 &\times \exp\left[\frac{1}{2} \left\{ B_{J_f J_2}^* + B_{J_f J'_2}^* + B_{J_i J_2} + B_{J_i J'_2} \right\}\right] \quad (51) \\
 &+ \Delta_{J_i J_2}^{(1)} \Delta_{J_f J'_2}^{(1)} \exp\left[B_{J_f J_2}^* + B_{J_i J_2}\right] ,
 \end{aligned}$$

where

$$\begin{aligned}
 S_{J_i J_f; J_2 J'_2}^{(2)middle} &= -\frac{1}{\pi^2} \sum_{k_1 k_2 k \mu} \frac{\sqrt{(2J_i + 1)(2J_f + 1)}}{(2k_1 + 1)(2k_2 + 1)} W\left(1 J_f J_i k_1; J_i J_f\right) \\
 &\times \langle J_i(0) k_1(0) | J_i(0) \rangle \langle J_f(0) k_1(0) | J_f(0) \rangle \langle J_2(0) k_2(0) | J'_2(0) \rangle^2 \\
 &\times \left| v_{k \mu}^{k_1 k_2} \left( \omega_{J_2} - \omega_{J'_2} \right) \right|^2 ,
 \end{aligned} \quad (52)$$

and we have

$$S(b) = 1 - \exp\left[B_{J_f J_2}^* + B_{J_i J_2}\right] + S_{J_i J_f; J_2}^{(2)corr} , \quad (53)$$

where

$$B_{J_1 J_2} = i \Delta_{J_1 J_2}^{(1)} - S_{J_1 J_2}^{(2)outer} - i \Delta_{J_1 J_2}^{(2)} + \Delta_{J_1 J_2}^{(1)2}/2 \quad (54)$$

and where  $s^{(2)\text{corr}}$  is given by equation (54) and  $\Delta^{(1)}$ ,  $s^{(2)\text{outer}}$ , and  $\Delta^{(2)}$  are given by equations (51), (49), and (50), respectively. Note that only  $s^{(2)\text{corr}}$  is sensitive to the decomposition of equation 21; the other terms in equation (53) do not depend on it at all.

It is appropriate at this time to remark on the similarity between our theory and Anderson's theory. Note that each of the quantities appearing in the above equations also appears in Anderson's theory. They appear, however, in a very different form.

#### 4. THE LINKED CLUSTER THEOREM

The following section is devoted to the simplification of the preceding results and the justification of the exponential expansion by use of a linked cluster theorem. We show first that matrix elements of the interaction between different vibrational states may be ignored as long as the potential contains the second- and higher-order forces from the outset. If this is the case, then the interaction Hamiltonian acts only on the rotational variables of the two molecules. We then show that we may separate certain terms from all orders of perturbation theory in the T-operator, and that the terms which are so separated may be summed to obtain the exponential expansion obtained earlier by a different method.

We first note that the above results simplify somewhat by observing that the Fourier transforms in equation (44) are negligible when

$$\omega \gg 2\pi v/b , \quad (55)$$

where  $v$  is the relative velocity of the collision and  $b$  is the collision impact parameter. Taking  $v = 3 \times 10^4$  cm/s and  $b = 5 \text{ \AA}$ , we obtain a typical value of  $20 \text{ cm}^{-1}$  for the cutoff frequency. This is comparable to the rotational splittings of a molecule, but it is very small compared to the splitting of the vibrational levels. Therefore, contributions to the sums in equations (52) and (46) from vibrational levels other than the ones corresponding to  $J_1, J_2$  may be neglected. For the same reason, electronic levels other than the ground level give no contribution to these sums.

For the  $\Delta^{(2)}$  term in equation (47), on the other hand, the situation is different. For large values of the energy denominator, the integral in (47) gives a contribution which is proportional to the inverse of the energy difference. In fact, the contribution to this term from the far-lying vibrational and electronic states is exactly what one would expect if the energy of interaction between the molecules were calculated according to Rayleigh-Schroedinger perturbation theory and added to  $V(t)$  to obtain an effective potential. This summing over the far-lying states may be performed to arbitrary order in perturbation theory and yields the well-known Van der Waals forces (induction, dispersion, etc.). We shall assume that these contributions have been included in the potential from the outset.

If we require that the higher-order forces are included in the potential, then we may therefore neglect all matrix elements of  $V$  between states of different vibrational and electronic quantum numbers; we therefore consider the potential to be a function only of the rotational variables of the two molecules, and we include the dependence of matrix elements on vibrational quantum numbers parametrically. Thus, in a given vibrational level, the potential contains as operators irreducible tensors which operate on the rotational variables of

molecules 1 and 2. This reduction of the vector space has been assumed implicitly in the preceding section; in particular, it means that all sums over intermediate states are actually over states that belong to the same electronic-vibrational manifold as the state under consideration.

This reduction of the vector space has another important consequence. To see this, we consider the expansion of  $V(t)$  into irreducible tensors as given by (37). We consider the product of several  $\tilde{V}$ 's:

$$P(t_1, t_2, \dots, t_n) = \tilde{V}(t_1) \tilde{V}(t_2) \dots \tilde{V}(t_n) . \quad (56)$$

Each of the factors in (56) is expandable in the form of equation 37; we consider the products obtained by taking one term from each factor. If the tensorial rank of the first factor is  $k_1^{(1)} k_2^{(1)}$ , the second  $k_1^{(2)} k_2^{(2)}$ , etc., where  $k_1^{(j)}$  is the rank of the  $j^{\text{th}}$  term in the space of molecule 1 and similarly for  $k_2^{(j)}$ , then the above product is a sum of terms, each of which is represented by the Kronecker product,

$$\left\{ D^{k_1^{(1)}} \times D^{k_1^{(2)}} \times \dots \times D^{k_1^{(n)}} \right\} \left\{ D^{k_2^{(1)}} \times D^{k_2^{(2)}} \times \dots \times D^{k_2^{(n)}} \right\} \\ = \sum_{k_1 k_2} a_{k_1 k_2} D^{k_1} D^{k_2} , \quad (57)$$

where the  $D^k$  are irreducible representations of the rotation group, and the coefficients  $a_{k_1 k_2}$  are determined by the properties of the rotation group. The product of potentials in equation (56) corresponds to the

sum of (57) over all allowable values of  $k_1^{(j)}$  and  $k_2^{(j)}$ . We shall be interested in separating out from this product all the terms which have  $k_1 = k_2 = 0$ ; i.e., the rotationally invariant part. Therefore, we write

$$P(t_1, t_2, \dots, t_n) = [\tilde{v}(t_1) \tilde{v}(t_2) \dots \tilde{v}(t_n)]^{(0)} +$$

(58)

$$+ [\tilde{v}(t_1) \tilde{v}(t_2) \dots \tilde{v}(t_n)]^i$$

where the first term corresponds to that portion of equation 57 with  $k_1 = k_2 = 0$ , and the remainder of equation (58) corresponds to (57) with values different from  $k_1 = k_2 = 0$ .

The first term of equation (58) has the important property that its matrix elements between any two states are diagonal in all quantum numbers. The fact that it is diagonal in the rotational quantum numbers follows from its rotational invariance ( $k_1 = k_2 = 0$ ); it is diagonal in vibrational and electronic quantum numbers because of our reduction of the vector space (i.e., separation of the higher-order forces).

With these preliminaries, we shall proceed with the derivation of the linked cluster theorem. We shall define a linked cluster of order  $n$  as a product of the form

$$[\tilde{v}(t_1) \tilde{v}(t_2) \dots \tilde{v}(t_n)]_L^{(0)} = P_L(t_1, t_2, \dots, t_n) \quad , \quad (59)$$

which contains no subproducts that transform like  $k_1, k_2 = (0,0)$ . According to the above, a product of the form  $[\tilde{v}(t_1) \tilde{v}(t_2) \dots \tilde{v}(t_n)]^{(0)}$ , which in general does contain subproducts which contain  $k_1 = k_2 = 0$  parts, may be broken up into parts which do not contain any  $k_1 = k_2 = 0$

parts; i.e., into a sum of products of linked clusters. For example, we have the product

$$\begin{aligned}
 & \left[ \tilde{v}(t_1) \dots \tilde{v}(t_m) \tilde{v}(t_{m+1}) \dots \tilde{v}(t_n) \right]^{(0)} \\
 &= \left[ \tilde{v}(t_1) \dots \tilde{v}(t_m) \right]^{(0)} \left[ \tilde{v}(t_{m+1}) \dots \tilde{v}(t_n) \right]^{(0)} \quad (60) \\
 &+ \left[ \tilde{v}(t_1) \dots \tilde{v}(t_m) \right]' \left[ \tilde{v}(t_{m+1}) \dots \tilde{v}(t_n) \right]' \dots
 \end{aligned}$$

The first term corresponds to a reduction of the original product into two similar products, which may themselves be reduced further. This procedure may be continued until it is impossible to reduce the clusters any further; that is, until every part of equation (60) which transforms according to  $k_1 = k_2 = 0$  is also a linked cluster. The second term in (60) is not reducible further as it stands, but may be reducible if arranged differently. This process may be continued until the entire product on the left-hand side of (60) has been broken up into a series of linked clusters.

We now consider equation (24) for the symmetric part of the T-matrix. We may substitute this relation into the power-series expansion (11) for the T-matrix, and arrive at the following expression:

$$\begin{aligned}
 \langle J_1 J_2 | | T^{00} | | J_1 J_2 \rangle &= \frac{1}{(2J_1 + 1)(2J_2 + 1)} \sum_{M_1 M_2} \sum_{n=0}^{\infty} \left( \frac{1}{i\hbar} \right)^n \\
 &\times \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{t_{n-1}} dt_n \langle J_1 M_1 J_2 M_2 | \tilde{v}(t_1) \dots \tilde{v}(t_n) | J_1 M_1 J_2 M_2 \rangle \quad (61)
 \end{aligned}$$

$$= \sum_{n=0}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{t_{n-1}} dt_n \quad (61)$$

$$\times \langle J_1 M_1 J_2 M_2 | \left[ \tilde{V}(t_1) \dots \tilde{V}(t_n) \right]^{(0)} | J_1 M_1 J_2 M_2 \rangle \quad .$$

In order to simplify what follows, we introduce the time-ordering operator  $T$ , which has the following property.

$$T f(t_1) f(t_2) = \begin{cases} f(t_1) f(t_2), t_1 > t_2 \\ f(t_2) f(t_1), t_1 < t_2 \end{cases} \quad (62)$$

Using this notation, we may write equation (61) as

$$\langle J_1 J_2 | | T^{00} | | J_1 J_2 \rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{1}{i\hbar}\right)^n \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{\infty} dt_n \quad (63)$$

$$\times \langle J_1 M_1 J_2 M_2 | \left[ T \tilde{V}(t_1) \dots \tilde{V}(t_n) \right]^{(0)} | J_1 M_1 J_2 M_2 \rangle \quad .$$

We now consider the effect of decomposing the right-hand side of this equation into linked clusters according to (60). We consider the decomposition of the  $n^{\text{th}}$  term into  $k_1$  linked clusters of order 1,  $k_2$  linked clusters of order 2, etc. The number of ways to do this is given by<sup>7</sup>

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<sup>7</sup>J. Hubbard, Proc. Roy. Soc., A240 (1957), 539.

$$w_{k_1 k_2 \dots} = \frac{n!}{k_1! k_2! \dots k_1! k_2! \dots} \quad , \quad (64)$$

and the total  $n^{\text{th}}$  order contribution to (65) is given by the sum of all such decompositions over all values of  $k_1, k_2, \dots$ , subject to the restriction

$$k_1 + 2k_2 + 3k_3 + \dots = n \quad . \quad (65)$$

When we perform the sum over  $n$  we obtain

$$\begin{aligned} \langle J_1 J_2 | | T^{00} | | J_1 J_2 \rangle &= \sum_{k_1 k_2 \dots} \\ &\times \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt_1 \langle J_1 M_1 J_2 M_2 | [\tilde{v}(t_1)]^{(0)} | J_1 M_1 J_2 M_2 \rangle^{k_1} \times \dots \end{aligned} \quad (66)$$

We may now remove the time-ordering operator, change back the integration limits, and perform the sum over the  $k$ 's to obtain the final expression

$$\begin{aligned} \langle J_1 J_2 | | T^{00} | | J_1 J_2 \rangle &= \exp \left[ \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt_1 \right] \\ &\times \langle J_1 M_1 J_2 M_2 | [\tilde{v}(t_1)]^{(0)} | J_1 M_1 J_2 M_2 \rangle + \left[ \frac{1}{i\hbar} \right]^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \\ &\times \langle J_1 M_1 J_2 M_2 | [\tilde{v}(t_1) \tilde{v}(t_2)]^{(0)} | J_1 M_1 J_2 M_2 \rangle + \dots \end{aligned} \quad (67)$$

Thus, we have rederived the exponential expansion in a different way. If we compare this result to equation (27), we see that the  $n^{\text{th}}$  order term in  $B$  is given by

$$B_{J_1 J_2}^{(n)} = \left(\frac{1}{i\hbar}\right)^n \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{t_{n-1}} dt_n \quad (68)$$

$$\times \langle J_1 M_1 J_2 M_2 | \tilde{v}(t_1) \dots \tilde{v}(t_n) \rangle_L^{(0)} | J_1 M_1 J_2 M_2 \rangle \quad .$$

By introducing our earlier notation into (68) we see that  $B^{(n)}$  is given by

$$B_{J_1 J_2}^{(n)} = \left(\frac{1}{i\hbar}\right)^n \frac{1}{(2J_1 + 1)(2J_2 + 1)} \sum_{\substack{J'_1 J'_2 J''_1 J''_2 \dots \\ \text{all } M}} \times \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{t_{n-1}} dt_n \left[ \langle J_1 M_1 J_2 M_2 | \tilde{v}(t_1) | J''_1 M''_1 J''_2 M''_2 \rangle \dots \right. \\ \left. \times \langle J'_1 M'_1 J'_2 M'_2 | \tilde{v}(t_n) | J_1 M_1 J_2 M_2 \rangle \right]_L \quad , \quad (69)$$

where again the subscript  $L$  indicates that only linked clusters are to be considered; that is, no subproduct of the matrix elements above contains a rotationally invariant part. This is a generalization of the Goldstone-Brueckner linked-cluster theorem<sup>7,8</sup> to degenerate systems.

<sup>7</sup>J. Hubbard, *Proc. Roy. Soc.*, A240 (1957), 539.

<sup>8</sup>J. Goldstone, *Proc. Roy. Soc.*, A239 (1957), 267.

The results given above may be exhibited explicitly for the second-order  $B_{J_1 J_2}^{(2)}$  from the formulas (45), (46), (47), and (48). In particular, the  $k_1 = k_2 = 0$  term of (47) gives no contribution, since the energy denominator  $\omega_{J_1 J_2} - \omega_{J_1'' J_2''}$  vanishes and since  $v_{00}^{00}(\omega)$  is an even function. The contribution to  $S_{J_1 J_2}^{(2)outer}$  from the term  $k_1 = k_2 = 0$  exactly cancels the term  $1/2\Delta^{(1)2}$  in (45). Therefore,  $B_{J_1 J_2}^{(2)}$  is given as in (71), the linked clusters being precisely the sums (46) and (47) with  $k_1 = k_2 = 0$  left out. We shall write these terms as  $S_{J_1 J_2}^{(2)outer'}$  and  $\Delta^{(2)'}$  respectively.

There is a further cancellation in  $S^{(2)corr}$  as given by equation (51), which arises from the  $k_1 = k_2 = 0$  part of the sum there. Therefore, the linked cluster theorem gives for the quantity  $S(b)$  to second order,

$$S(b) = 1 - \exp \left[ B_{J_f J_2}^* + B_{J_1 J_2} \right] + S_{J_1 J_f; J_2}^{(2)corr} , \quad (70)$$

where

$$S_{J_1 J_f; J_2}^{(2)corr} = \sum_{J'_2} S_{J_1 J_f; J_2 J'_2}^{(2)middle'} \quad (71)$$

$$\times \exp \left[ \frac{1}{2} \left\{ B_{J_f J_2}^* + B_{J_f J'_2}^* + B_{J_1 J_2} + B_{J_1 J'_2} \right\} \right] ,$$

where  $S_{J_1 J_f; J_2 J'_2}^{(2)middle'}$  is as given in equation (52) with the  $k_1 = k_2 = 0$  part omitted, and where

$$B_{J_1 J_2} = -i\Delta_{J_1 J_2}^{(1)} - S_{J_1 J_2}^{(2)outer'} - i\Delta_{J_1 J_2}^{(2)'} . \quad (72)$$

The linked cluster theorem has provided both an alternative way to derive the exponential expansion and also a simplification of the theory, having eliminated extraneous terms from our equations (45), (46), (47), (48), and (49). Of course, we could have noticed this cancellation without going through the laborious procedure of deriving the linked cluster theorem. However, our derivation has two advantages; first, it gives a much simpler formula (69) for the higher-order  $B^{(n)}$ 's and second (and more important), it provides us with some insight into the nature of the exponential expansion and its relation to more familiar expansions of this type used in other branches of physics.

## 5. COMPARISON TO EARLIER IMPACT THEORIES

It is easy to show that the earlier impact theories follow directly from the one presented here, given certain approximations. The simplest of these is the old phase-shift theory,<sup>9</sup> which follows directly from (70). If we consider an intermolecular potential which contains no angular dependence whatsoever--that is, if the potential contains only  $k_1 = k_2 = 0$  in the decomposition into irreducible tensor operators--then our reduction of the vector space and the linked cluster theorem implies that all the  $B_{J_1 J_2}^{(n)}$  vanish except the first-order contribution, and all the  $A^{(n)}$  vanish except  $A^{(0)}$ . In this case, we have

$$B_{J_1 J_2}^{\text{phase shift}} = -i\Delta_{J_1 J_2}^{(1)} \quad (73)$$

and furthermore,

$$S(b)^{\text{phase shift}} = 1 - e^{-i\Delta} \quad , \quad (74)$$

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<sup>9</sup>V. F. Weisskopf, *Phys. Zeits.*, 34 (1933), 1.

where

$$\eta = \Delta_{J_i J_2}^{(1)} - \Delta_{J_f J_2}^{(1)} . \quad (75)$$

This is the familiar phase shift result.<sup>9</sup>

If we carry this type of analysis further, we may consider cases in which the potential contains terms with some angular dependence. In this case, we also consider the phase shift separately, but this time we obtain higher-order contributions, which consist of all the imaginary parts of the various  $B_{J_1 J_2}$ :

$$\begin{aligned} \eta &= \text{Im } B_{J_f J_2} - \text{Im } B_{J_i J_2} \\ &= \Delta_{J_i J_2}^{(1)} - \Delta_{J_f J_2}^{(1)} + \Delta_{J_i J_2}^{(2)} - \Delta_{J_f J_2}^{(2)} . \end{aligned} \quad (76)$$

At the same time we consider the other effects of the nonisotropic part of the potential. One such effect is the reorientation of the radiating molecule; the second is the possibility of an inelastic collision.<sup>5</sup> If we single out all the terms in  $B_{J_1 J_2}$  which have intermediate states of the radiator which differ from  $J_1$ , then we may factor these out from  $S(b)$  in the following manner:

$$P_{el} = \exp \left[ \text{Re} (B_{J_f J_2} + B_{J_i J_2}) \right] . \quad (77)$$

In order to obtain a simple expression for the rest of the terms, we shall make the approximation that in equation (71) the terms  $B_{J_f J_1}$  and  $B_{J_i J_2}$ , respectively. This is a good approximation since  $S^{(2)corr}$  is

<sup>5</sup>R. G. Gordon, *J. Chem. Phys.*, 44 (1966), 3. 3.

<sup>9</sup>V. F. Weisskopf, *Phys. Zeits.*, 34 (1933), 1.

small to begin with, and since the nonresonant terms in which this approximation is made are small compared with the resonant terms. Also, the  $B_{J_1 J_2}$  factors are not expected to be strong functions of  $J_2$ . With this in mind, the part of  $S(b)$  which has not yet been factored out may be written as:

$$\cos^2(\alpha/2) = \exp \left[ \operatorname{Re} \left( B''_{J_f J_2} + B''_{J_i J_2} \right) \right] \quad (78)$$

$$\times \left[ 1 - \sum_{J'_2} S_{J_i J_f; J'_2 J'_2}^{(2) \text{middle}} \right] .$$

In equation (77),  $B'_{J_1 J_2}$  represents the part of  $B_{J_1 J_2}$  which contains intermediate states of the radiating molecule which differ from  $J_1$ , and in (78)  $B''_{J_1 J_2}$  represents that part of  $B_{J_1 J_2}$  which contains no such states. Clearly, equation (77) represents effects of inelastic collisions, whereas equation (78) represents effects of reorientation.

Using equations (76), (77), and (78), we may write equation (70) as

$$S(b) = 1 - p_{el} e^{-in} \cos^2(\alpha/2) , \quad (79)$$

which is of the same form as Gordon's semiclassical expression for  $S(b)$ . With this in mind, we shall interpret  $p_{el}$  as the probability of an elastic collision and  $\alpha$  as the angle through which the angular momentum is reoriented by the collision. In fact, if one were to make a power series of equations (76) through (78), one would recover Gordon's

equations (42 a) through (42 c), in which Gordon's theory is compared with Anderson's theory. The theory presented here is therefore, in some senses, a quantum-mechanical version of Gordon's semiclassical theory. It gives the three terms in (79) in their correct relationship to one another; that is, it gives factors in a product rather than as three separate additive terms, as Anderson's theory does.<sup>1</sup>

On the other hand, one may obtain Anderson's theory simply by making a power-series expansion of (70) in the interaction potential. Such an expansion gives

$$S(b) = 1 - \left[ 1 + i\Delta_{J_f J_2}^{(1)} - i\Delta_{J_i J_2}^{(1)} - \frac{1}{2} \left( \Delta_{J_f J_2}^{(1)} - \Delta_{J_i J_2}^{(1)} \right)^2 \right. \\ \left. - S_{J_f J_2}^{(2)outer'} - S_{J_i J_2}^{(2)outer'} + i\Delta_{J_f J_2}^{(2)} - i\Delta_{J_i J_2}^{(2)} \right] + \sum_{J_2'} S_{J_i J_f; J_2' J_2}^{(2)middle'} . \quad (80)$$

There is considerable cancellation in the above result, since  $S_{J_1 J_2}^{(2)outer'} + \frac{1}{2} \Delta_{J_1 J_2}^{(1)2} = S_{J_1 J_2}^{(2)outer}$  and since

$$S_{J_i J_f; J_2' J_2}^{(2)middle'} - \delta_{J_2' J_2} \Delta_{J_f J_2}^{(1)} \Delta_{J_i J_2}^{(1)} = S_{J_i J_f; J_2' J_2}^{(2)middle} . \quad (81)$$

Therefore, the effect of the expansion is to remove the primes from the  $S^{(2)}$  terms, and we are left with the result

$$S(b) = i\Delta_{J_i J_2}^{(1)} - i\Delta_{J_f J_2}^{(1)} + S_{J_i J_2}^{(2)outer} + S_{J_f J_2}^{(2)outer} \\ + \sum_{J_2'} S_{J_i J_f; J_2' J_2}^{(2)middle} + i\Delta_{J_i J_2}^{(2)} - i\Delta_{J_f J_2}^{(2)} . \quad (82)$$

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<sup>1</sup>P. W. Anderson, *Phys. Rev.*, 76 (1949), 647.

This is the expression given by Anderson, modified by the second-order phase shift introduced by Sharma and Caledonia.<sup>3</sup> The fact that it is derivable from our theory should not be surprising, since both theories were obtained from the same theoretical framework. We note also that if one further term were kept in the expansion, the phase shifts would be multiplied by the same cutoff used by Sharma and Caledonia<sup>3</sup> for the imaginary part of  $S(b)$ .

Equation (70), however, is more than a simple rearrangement of the Anderson theory; it contains a natural cutoff. The theory of Murphy and Boggs<sup>4</sup> also contains a cutoff, and in fact the interruption function obtained by Murphy and Boggs is equal to, in our notation,

$$S(b)_{\text{Murphy-Boggs}} = 1 - \frac{1}{2} \left[ \exp(2B_f^* J_2) + \exp(2B_i J_2) \right], \quad (83)$$

which has some similarity to our form but which suffers from several defects. First of all, the reorientation effects are neglected; i.e., the  $S^{(2)\text{middle}}$  term is entirely absent from (83). Second, equation (83) contains the effects of initial and final states in an additive rather than the correct multiplicative manner. Finally, the isotropic part of the interaction is completely absent from (83), which makes the Murphy-Boggs theory totally inapplicable to rotation-vibration spectra. The last defect is partially a result of the ad hoc manner in which  $M$ -averaging is performed in the theory.

We have compared our theory to the major theories of impact broadening and shifting. Our theory reduces to these in the appropriate limits. For isotropic interactions, we arrive at the phase-shift theory. We have arranged the terms in the theory so that they

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<sup>3</sup>R. D. Sharma and G. E. Caledonia, *J. Chem. Phys.*, 54 (1970), 434.

<sup>4</sup>J. S. Murphy and J. E. Boggs, *J. Chem. Phys.*, 47 (1967), 691.

correspond to terms in Gordon's theory. By expanding out our results, we have arrived at Anderson's theory. We have shown that our result is similar to the Murphy-Boggs theory, although we cannot reproduce Murphy-Boggs theory, as we have reproduced the others. In the next section we shall compare numerical results obtained with our theory with those obtained with the most important of the others, the Anderson theory.

## 6. THEORY AND CALCULATIONS

In this section we comment on some aspects of the theory and perform calculations. In particular, we shall show the connection between our linked cluster theorem and the Goldstone-Brueckner theorem<sup>8</sup> by the familiar diagrammatic approach. We shall compare the cutoff obtained here to the cutoff introduced by Anderson. We shall calculate the real and imaginary parts of the broadening cross section in closed form for a highly idealized case. Finally, we shall calculate the HC1 self-broadening half-widths exactly for the 0 to 2 vibrational band.

### 6.1 Diagrammatic Representation

It is possible using a diagrammatic representation of the intermolecular interaction to establish further the connection between the linked cluster theorem obtained here and the more familiar theorems associated with the many-body problem.<sup>7,8</sup> In particular, consider the simple interaction vertex shown in figure 1(a). This diagram shows two solid lines representing molecular states, and a wavy line representing an external field. Conservation of angular momentum at each vertex implies that

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<sup>7</sup>J. Hubbard, *Proc. Roy. Soc.*, A240 (1957), 539.

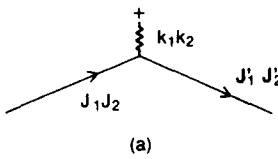
<sup>8</sup>J. Goldstone, *Proc. Roy. Soc.*, A239 (1957), 267.

$$\begin{array}{c} J \\ \sim_1 \end{array} + \begin{array}{c} k \\ \sim_1 \end{array} = \begin{array}{c} J' \\ \sim_1 \end{array} \quad (84 \text{ a})$$

$$\begin{array}{c} J \\ \sim_2 \end{array} + \begin{array}{c} k \\ \sim_2 \end{array} = \begin{array}{c} J' \\ \sim_2 \end{array} \quad . \quad (84 \text{ b})$$

This relation gives the usual triangular inequalities. When constructing more complicated diagrams, we must sum over all the M-quantum numbers in closed loops.

The invariant part of the T-matrix element is given by the sum over all possible closed-loop diagrams, as shown in figure 1(b). Note that some of these diagrams are disconnected. The linked cluster theorem proved earlier implies the factorization of such diagrams; the factorization is such that  $B_{J_1 J_2}$  (see equation (26)) contains no disconnected parts, as shown in figure 1(c).



(a)

$$\langle J_1 J_2 \parallel T^{00} \parallel J_1 J_2 \rangle = 1 + \text{Diagram (b)} + \text{Diagram (b)} + \dots$$

(b)

$$B_{J_1 J_2} = \text{Diagram (c)} + \text{Diagram (c)} + \dots$$

(c)

Figure 1. Diagrammatic representation of intermolecular interaction:  
 (a) basic interaction vertex, in which solid lines represent the two-molecule state. Wavy line represents external field; (b) expansion of isotropic part of T-matrix, which includes the unlinked graphs; (c) expansion of B given by linked cluster theorem, in which unlinked graphs are absent.

## 6.2 Shape of $S(b)$

It is of interest to investigate the differences between the exponential cutoff derived here and the straight-line cutoff given by Anderson.<sup>1,2</sup> The interruption functions are shown for a typical case in figure 2. It can be seen that over most of the range of impact parameter, the exponential cutoff yields a value for  $ReS(b)$  which is less than Anderson's  $ReS(b)$ . The oscillation of  $S(b)$  about the value unity for small  $b$  does not occur in all cases and is exaggerated here for emphasis. In general, it is a very small effect unless the phase-shift terms completely overwhelm the  $S^{(2)outer}$  terms.

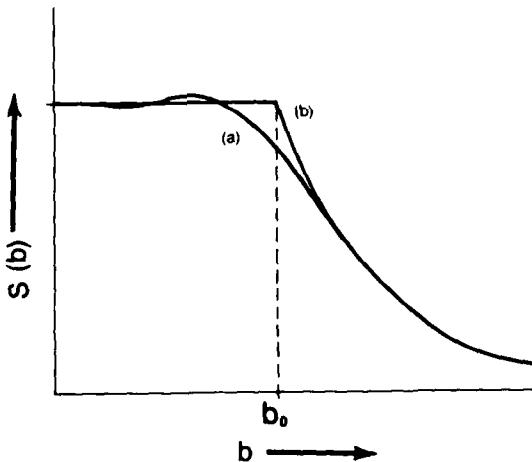


Figure 2. Shape of interruption function: curve (a) this work, curve (b) Anderson theory.

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<sup>1</sup>P. W. Anderson, *Phys. Rev.*, 76 (1949), 647.

<sup>2</sup>P. W. Anderson, *PhD Dissertation, Harvard University (1949)*.

### 6.3 Evaluation of Cross Sections for Special Cases

Under certain conditions, the integral of  $S(b)$  over the impact parameter may be performed in closed form. This will be true in general if

(1) A given term in the potential dominates all other terms,  
and

(2) For these terms, the only important contributions to  $S(b)$  are the Stark and resonance terms.

Under these conditions, the only nonzero factors in  $S(b)$  are  $\Delta^{(1)}$ , the first-order phase shift, and  $S^{(2)\text{outer}}$ , the second-order broadening term. Each of these terms will be proportional to some power of the impact parameter.

The largest terms in the potential which contribute to  $\Delta^{(1)}$  are the induction and dispersion terms, which are proportional to the inverse sixth power of the intermolecular distance. We may write

$$V_{000}(R) = -A/R^6 , \quad (85)$$

where the constant  $A$  depends on the vibrational quantum numbers. The integral (41) for the first-order phase shift may be readily evaluated for this potential to give

$$\Delta^{(1)} = -3\pi A/(8\hbar v b^5) . \quad (86)$$

To evaluate  $S^{(2)\text{outer}}$  we consider as an example the dipole-dipole interaction between two linear molecules. We may write this interaction in terms of spherical tensors as

$$v_{d-d} = \frac{\sqrt{6}\mu_1\mu_2}{R^3} \sum_{m_1 m_2} C_{1m_1}^{(1)} C_{1m_2}^{(2)} \times C_{2,m_1+m_2}^{\dagger} \hat{R} \langle 1(m_1) 1(m_2) | 2(m_1 + m_2) \rangle \quad (87)$$

and therefore we have, from equation (36),

$$v_{112}(R) = \sqrt{6} \mu_1 \mu_2 / R^3 \quad (88)$$

Now the summation may be performed in (46) using this potential, and the integrals in (44) may be evaluated to give<sup>6</sup>

$$S_{J_1 J_2}^{(2)\text{outer}} = \frac{4}{9} \left( \frac{\mu_1 \mu_2}{\pi R^3} \right)^2 \sum_{J'_1 J'_2} \langle J_1(0) 1(0) | J'_1(0) \rangle^2 \times \langle J_2(0) 1(0) | J'_2(0) \rangle^2 f_1(k) \frac{1}{b^4} \quad (89)$$

where

$$f_1(k) = \frac{1}{4} k^4 \left[ K_2^2(k) + 4K_1^2(k) + 3K_0^2(k) \right] \quad (90)$$

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<sup>6</sup>C. J. Tsao and B. Curnutte, *J. Quant. Spectr. Rad. Trans.*, 2 (1962), 41.

and where

$$k = (\omega_{J'_1 J'_2} - \omega_{J_1 J_2})^{b/v} . \quad (91)$$

The V-C coefficients vanish for Stark splitting ( $J_1 = J'_1$ ,  $J_2 = J'_2$ ). If, however, the molecules are identical, then one may obtain  $k = 0$  by setting  $J_2 = J'_1$  and  $J'_2 = J_1$  (resonance). We shall assume that all other contributions are small compared to the resonance contribution. In this case, since  $f_1(k)$  is unity for  $k = 0$ , we obtain:

$$S_{J_1 J_2}^{(2)\text{outer}} = \frac{4}{9} \left( \frac{\mu_1 \mu_2}{\hbar v} \right)^2 \frac{1}{b^4} \langle J_1(0) 1(0) | J_2(0) \rangle^2 \langle J_2(0) 1(0) | J_1(0) \rangle^2 , \quad (92)$$

where  $J_2 = J_1 \pm 1$ . Since the second-order phase shift vanishes on resonance, and since the  $S_{J_1 J_2}^{(2)\text{middle}}$  term vanishes for dipole-dipole interactions, we have determined all contributions to  $S(b)$  and we may write

$$S(b) = 1 - \exp \left[ -i \left( a_0/b \right)^5 - \left( b_0/b \right)^4 \right] , \quad (93)$$

where  $a_0$  and  $b_0$  are given in terms of the coefficients in  $\Delta^{(1)}$  and  $S_{J_1 J_2}^{(2)\text{outer}}$ .

Using the expression (92) in equation (4), the resulting integral may not be evaluated in closed form. However, if  $a_0 \ll b_0$ , we may expand the imaginary part of the exponential to obtain

$$\sigma \approx 2\pi \int_0^\infty b \, db \left\{ 1 - e^{-\left(b_0/b\right)^4} + i \left(a_0/b\right)^5 e^{-\left(b_0/b\right)^4} \right\} . \quad (94)$$

Evaluation of the integral yields

$$\sigma = 2\pi b_0^2 \left\{ \frac{1}{2} \Gamma\left(\frac{1}{2}\right) + i \frac{1}{4} \Gamma\left(\frac{3}{4}\right) \left(a_0/b_0\right)^5 \right\} \quad (95)$$

$$= 2\pi b_0^2 \left\{ (0.8862) + i(0.3064) \left(a_0/b_0\right)^5 \right\} .$$

On the other hand, we may use the Sharma-Caledonia<sup>3</sup> cutoff in the Anderson theory to obtain

$$\sigma_A = 2\pi \int_{b_0}^{\infty} b \, db \left\{ \left(b_0/b\right)^4 + i \left(a_0/b\right)^5 \left[ 1 - \left(b_0/b\right)^4 \right] \right\} , \quad (96)$$

which may be evaluated to yield

$$\sigma_A = 2\pi b_0^2 \left\{ 1 + i \frac{4}{33} \left(a_0/b_0\right)^5 \right\} \quad (97)$$

$$= 2\pi b_0^2 \left\{ 1 + i(0.1905) \left(a_0/b_0\right)^5 \right\} .$$

Thus, there is a 10-percent difference between the real parts of the cross section in the two theories, whereas Anderson's imaginary part is a factor of 1.6 lower than ours. If we consider velocity averaging, this will increase the imaginary part of the cross section by a factor of 1.33 in both theories, but will have no effect on the real part of the cross section.

#### 6.4 Exact Calculation for HCl Self-Broadening

As an illustration of the theory, we have performed exact calculations of the self-broadening in the 0 to 2 vibrational band of HCl. Interactions considered in the calculation were the dipole-dipole, dipole-quadrupole, quadrupole-dipole, quadrupole-quadrupole, dipole-octupole, and octupole-dipole interactions. Also considered were the isotropic parts of the induction and dispersion interactions, for which the difference of coefficients  $A$  in  $-A/r^6$  was taken to be  $12280 \text{ cm}^{-1} \text{ \AA}^6$ . Other contributions to the interatomic potential (which may be important for foreign gas broadening or for cases where there is no permanent dipole moment) were neglected.

Contributions to  $S(b)$  from the various interactions were computed as in Tsao and Curnutte<sup>6</sup> and Isnard et al.<sup>10</sup> Equation (79) was used for  $S(b)$ . Molecular parameters used in the calculation are those given in table 1. The quantities  $\mu$ ,  $\Theta$ ,  $\Omega$ , and  $B$  are, respectively, the dipole moment, quadrupole moment, octupole moment, and rotational energy constant. Results of the calculation are shown in table 2 and figure 3. In the table,  $|m|$  is equal to  $\max(J_i, J_f)$  according to the usual notation. We also show the results of a calculation using the same parameters and using the Anderson cutoff. The experimental numbers are an average of the data given in Toth et al.<sup>11</sup> and Smith et al.<sup>12</sup>

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<sup>6</sup>C. J. Tsao and B. Curnutte, *J. Quant. Spectr. Rad. Trans.*, 2 (1962), 41.

<sup>10</sup>P. Isnard, C. Boulet, and A. Levy, *J. Quant. Spectr. Rad. Trans.*, 13 (1973), 1433.

<sup>11</sup>R. A. Toth, R. E. Hunt, and E. K. Plyer, *J. Mol. Spectr.*, 35 (1970), 110.

<sup>12</sup>A. Levy, E. Piollet, J. P. Bouanich, and C. Haeusler, *J. Quant. Spectr. Rad. Trans.*, 10 (1970), 203.

TABLE 1. MOLECULAR PARAMETERS USED IN THE CALCULATIONS

Quantity	Upper* state	Lower* state
$\mu$ (D)	1.167	1.108
$\theta$ (D-Å)	3.93	3.60
$\Omega$ (D-Å <sup>2</sup> )	4.0	4.0
$B$ (cm <sup>-1</sup> )	9.828	10.440

\*Values of the dipole moment were taken from Smith.<sup>13</sup> The equilibrium value for the quadrupole moment is DeLeeuw and Dynamus,<sup>14</sup> and the first term in its vibrational dependence is from Friedmann and Kimel.<sup>15</sup> The value of the octupole moment is taken from Sharma and Caledonia<sup>3</sup> it is just an estimate, but seems much more reasonable than that of Isnard et al.<sup>10</sup> Rotational constants are from Smith.<sup>13</sup>

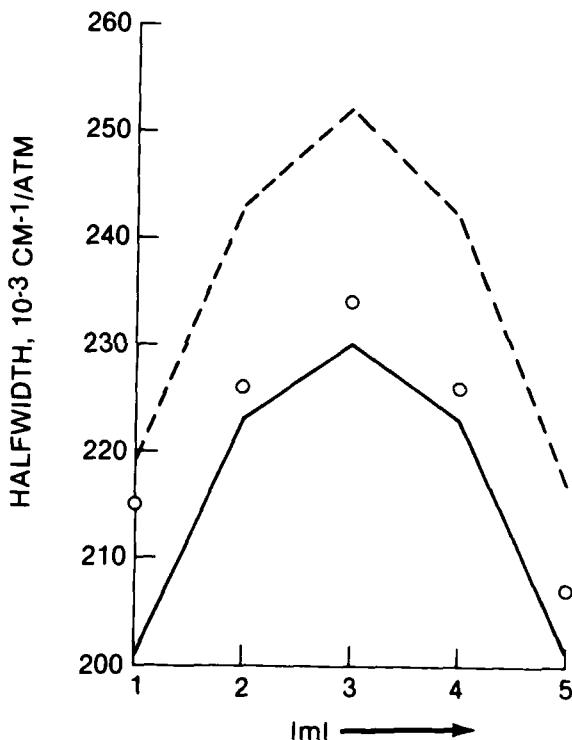
Figure 3. Self-broadened halfwidths of HCl: Solid line, this work. Dashed line, Anderson cutoff. Circled points, experimental data of Toth et al.<sup>11</sup> and Levy et al.<sup>12</sup>

TABLE 2. COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS FOR HCl SELF-BROADENING

Units for widths are 10<sup>-3</sup> cm<sup>-1</sup>/atm.

m	Experiment <sup>11,12</sup>	Calculation*	
		This work	Anderson theory
1	215	201	219
2	226	223	243
3	234	230	252
4	226	223	242
5	207	201	217

\*Calculated using the interactions described in the text. Molecular parameters are given in table 1.



<sup>3</sup>R. D. Sharma and G. E. Caledonia, *J. Chem. Phys.*, 54 (1970), 434.

<sup>10</sup>P. Isnard, C. Boulet, and A. Levy, *J. Quant. Spect. Rad. Trans.*, 13 (1973), 1433.

<sup>11</sup>R. A. Toth et al, *J. Mol. Spect.*, 35 (1970), 110.

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<sup>14</sup>F. H. DeLeeuw and A. Dynamus, *J. Mol. Spect.*, 48 (1973), 427.

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Agreement between our theory and the experimental data is excellent; moreover, it is much better than the agreement between Anderson's theory and experiment. In earlier calculations<sup>10</sup> using the Anderson theory, it was necessary to invoke an abnormally large value of the octupole moment ( $15 \text{ D}\text{-}\text{\AA}^2$ ) in order to match the experimental results.

## 7. CONCLUSIONS

A theory of impact broadening and shift has been developed which combines the best features of the Anderson, Gordon, and Murphy-Boggs theories in that it uses Anderson's expression for  $S(b)$  (equation (6)), which is exact in the impact limit and employs an exponential expansion of the T-matrix to ensure convergence of integrals over the impact parameter. The final form for  $S(b)$  contains only terms which are in the Anderson theory, but these terms are arranged in such a way that the final form (79) for  $S(b)$  is similar to that of Gordon. Evaluation of the broadening and shift cross sections for certain simple cases shows that whereas the broadening is not particularly sensitive to the cutoff procedure, the shift is. Similar conclusions apply to the influence of velocity averaging. Calculation of broadening parameters exactly for HCl self-broadening indicates significant improvement over calculations performed using Anderson's theory.

## ACKNOWLEDGEMENTS

One of us (D. Korff) is grateful to Robert Center of A.E.R.L. for suggesting the problem which led to the present work. The other (R. Leavitt) is grateful to Clyde A. Morrison of Harry Diamond Laboratories for useful comments on this work. We are both indebted to Hans Bethe for his invaluable suggestions and comments.

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